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(71)(72) Applicant and Inventor: <b>HELLER, Adam [US/US]; 5317 Valbum Circle, Austin, TX 78731 (US).</b>			
(72) Inventors; and (75) Inventors/Applicants (for US only): <b>PAZ, Yaron [IL/US]; 620 West 51st Street #105, Austin, TX 78751 (US). HARUVY, Yair [IL/IL]; 7 KKL Street, 76345 Rehovot (IL).</b>			
(74) Agent: <b>KETTELBERGER, Denise, M.; Merchant, Gould, Smith, Edell, Welter &amp; Schmidt, 3100 Norwest Center, 90 South Seventh Street, Minneapolis, MN 55402 (US).</b>		<b>Published</b> <i>With international search report.</i>	

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(54) Title: **SELF-CLEANING GLASS AND METHOD OF MAKING THEREOF**

(57) Abstract

A self-cleaning glass, usable, for example, as a window or windshield, coated with an optically clear and abrasion resistant film comprising a photocatalyst is formed on common glass by depleting alkali metal oxides from the glass and/or by forming a barrier to the migration of such oxides from the glass into the photocatalyst-containing coating. Upon exposure to light absorbed by the photocatalyst and in the presence of air, the film strips grime and contaminants from the glass surface.

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## SELF-CLEANING GLASS AND METHOD OF MAKING THEREOF

## Field of Invention

This invention relates to the photocatalytic oxidative stripping of organic  
5 contaminants from the surface of glass and the process of making such photocatalytic  
glass.

## Background of the Invention

It has been known for some time that photocatalysts, particularly titanium  
10 dioxide in the anatase phase, accelerate the air-oxidation of organic compounds upon  
exposure to light, usually ultraviolet, absorbed by the photocatalyst. See, for example,  
*Photocatalytic Purification of Water and Air*, D.F. Ollis and H. Al-Ekabi, eds.,  
Proceedings of the First International Conference on TiO<sub>2</sub> Photocatalytic Purification and  
Treatment of Water and Air, London, Ontario, Canada, 1993, Elsevier, Amsterdam. The  
15 major sections of the book describe the theory and fundamentals of titanium dioxide  
(TiO<sub>2</sub>) photocatalysis, photocatalyzed water and air treatment, reactor design and  
photocatalytic oxidation process economics. In all of these applications the photocatalyst  
is bound to a ceramic substrate to which it adheres. For example, on page 123, R. W.  
Mathews describes TiO<sub>2</sub> coated glass mesh and TiO<sub>2</sub> coated glass tube-based  
20 photoreactors. Another reactor with a TiO<sub>2</sub> coated glass tube is described by T. Ibusuki et  
al. on page 376. The photocatalytic films described were all light scattering, as they were  
made of photocatalysts such as Degussa P25, e.g., with an abundance of titanium dioxide  
particles approximately 0.1-0.3 microns in diameter. This particle size, even in the  
thinnest films, produces a milky appearance. Such light scattering films are not efficient  
25 or useful in applications such as clear, self-cleaning glass surfaces for windows and  
mirrors.

It is also known that clear and adherent, non-light scattering TiO<sub>2</sub> films can  
be made. Such known films are applied to optical lenses of optical instruments to provide  
scratch resistance and are also applied in anti-reflective optical coatings, usually by  
30 reactive evaporation or by reactive sputtering of titanium in an oxygen-containing  
atmosphere. Such coatings can also be made by applying a solution containing a  
precursor of a photocatalyst, e.g., TiO<sub>2</sub>, to a glass surface, forming a precursor film and

heating to a high temperature where organic matter in the precursor film is oxidized and  $\text{TiO}_2$  is crystallized. However, on substrates consisting of glasses comprising more than about 10% by weight of combined alkali metal oxides, particularly sodium oxide ( $\text{Na}_2\text{O}$ ) and potassium oxide ( $\text{K}_2\text{O}$ ), these films are poor photocatalysts, i.e., when exposed to sunlight in air they do not oxidize organic contaminants at a rate adequate to maintain a clean glass surface. For example, when coated with a film of stearic acid, they oxidize it under  $2.4 \text{ mWcm}^{-2}$  365 nm irradiance at a rate of 4nm per hour or less, i.e., reduce the thickness of the stearic acid film by less than 4nm per hour. Under the same conditions, a good photocatalyst strips a film of stearic acid at a rate of about 20nm per hour or more, i.e., reduces the thickness of the stearic acid film by about 20 nm per hour (or more).

It has now been found that migration of sodium into the photocatalytic film, (e.g., leaching out of common soda lime glass), particularly during the formation of the film from precursors, results in severely reduced activity of the photocatalytic films and reduced photocatalytic efficiency of self-cleaning glass. It would be highly advantageous to provide a means for reducing the deleterious effects of migrating alkali metal oxides and/or sodium on the photoactivity of self-cleaning, photocatalytic film-coated glasses.

### Summary of the Invention

We have discovered a barrier to the migration of alkali metal oxides from a glass substrate into the photocatalytic coating that is thin, yet effective. This barrier layer slows or blocks the migration of alkali metal oxides into the photocatalyst layer during its formation from a precursor and also after its formation from the precursor.

The preferred barrier is formed by first introducing into the near surface region of the glass to be coated, protons, i.e. hydrogen ions, by exchanging alkali metal ions with protons of an acid and/or by hydrolytic cleavage of silicon-oxygen-silicon bonds with an acid, in a process called "acid etching" or simply "etching". The hydrogen or proton-containing glass layer is then reacted with a precursor of an oxide of a four-valent element, preferably a precursor of crystalline titania or zirconia comprising inorganic oxide. In this process, a thin, sodium-migration blocking layer comprising titanium, silicon and oxygen and/or zirconium, silicon and oxygen is formed.

A sodium migration blocking layer is also formed when the proton or hydrogen-containing glass (acid glass), is reacted with a precursor of silica. A preferred process of forming the acid glass layer includes etching with acid, most preferably boiling in 9 M sulfuric acid. The sodium migration reducing barrier layer is preferably formed upon heating the acid glass with a precursor of titania, and/or zirconia to a temperature in excess of about 300°C and less than about 500°C and preferably about 400°C.

The photocatalytic activity of a formed, optically clear  $\text{TiO}_2$  layer on glass is also enhanced by treating the  $\text{TiO}_2$  coated glass with a material that reacts with sodium oxide, particularly with a dilute acid that does not dissolve  $\text{TiO}_2$  in the form in which it is included in the coating. In general, the anion of an acid that does not dissolve  $\text{TiO}_2$  does not form a strong complex with four valent titanium. These types of acids include protic acid, Lewis acid and Bronsted acid, and can be in liquid or gas form. For example, nitric, perchloric, and tetrafluoroboric acids are useable in the invention, as they are not known to form complexes with four valent titanium. Chlorides, fluorides and sulfates are generally not useable in the invention because they are known to strongly complex with titanium (IV).

The imposition of a sodium migration blocking layer on the surface of a sodium containing glass, e.g., common soda lime glass, assures formation of the desired photocatalytic anatase phase by prohibiting migration of sodium from the glass and into the precursor of the photocatalytic film. This barrier also reduces sodium contamination of the anatase phase that lowers the photocatalytic activity. A particularly useful sodium migration blocking layer is formed by applying a film of an organotitanate that decomposes upon heating in air, a nascent, yet non-crystalline precursor of anatase  $\text{TiO}_2$ , and reacting the precursor with the sodium-depleted acid glass prior to final calcining of the coated glass and at an elevated temperature, preferably about 450°C. After final calcination, a transparent, non-scattering, adherent nanocrystalline photocatalytic oxide film is produced, with a distinct, sodium migration-blocking interface between the glass and the photocatalytic film.

The photocatalyst coated glass of the invention, when exposed to ultraviolet light, efficiently cleans itself of organic contaminants. This photocatalyst coated glass of the invention is particularly useful in applications such as photocatalytically self-cleaning windows, windshields and mirrors.

### Brief Description of the Figures

Figure 1 is a graph showing the UV absorption spectra of  $\text{TiO}_2$  films on fused silica.

Figure 2 is FTIR spectra of stearic acid coated on clear  $\text{TiO}_2$  film on fused silica prior to (dotted line) and after (solid line) exposure to UVA light for 7.5 minutes.

Figure 3 is a graph showing the UV absorption spectra of  $\text{TiO}_2$  films on etched (dashed line) and on non-etched soda lime glass (solid line).

Figure 4 is a graph showing the effect of the calcination temperature on UVA, i.e., near UV, photoactivity of clear films of titanium dioxide: (A) Two layers of  $\text{TiO}_2$  on fused silica, (B) Two layers of  $\text{TiO}_2$  on etched glass, (C) One layer of  $\text{TiO}_2$  on etched glass, (D) One layer of  $\text{TiO}_2$  on one layer of  $\text{ZrO}_2$  on etched glass.

Figure 5 is a graph showing the effect of etching duration on the photoefficiency of clear  $\text{TiO}_2$  films on soda lime glass.

### Detailed Description of the Preferred Embodiment

The invention is directed toward self-cleaning glass and methods of making the same. Photocatalytic films can form the basis for self-cleaning or photooxidatively cleaning glass, useful, for example, as self-cleaning windows, mirrors, optical components, eyeglass lenses, and automotive windshields. When using photocatalyst films, e.g.  $\text{TiO}_2$ , in these applications, the following should be optimized: the absence of scattering of visible light; abrasion resistance to an extent that the film is typically not damaged when cleaned or when impacted by dust particles; and an adequate photooxidation rate or efficiency in order to maintain a relatively clean glass surface. The coated self-cleaning glasses of the invention provide an abrasion resistant, photoefficient, optically clear, self-cleaning glass.

Deposition of organic contaminants on glass usually reduces visibility. Furthermore, light particularly from headlights of oncoming cars and from the sun when the sun is low on the horizon, interferes with driving when the windshield is contaminated. Films of organic contaminants smeared on the windshield by wipers operating in rain also add to the hazard of driving. Light scattered from contaminants on outside or inside rearview mirrors of cars impairs visibility in these mirrors. Dirt or fingerprints on lenses

or eyeglasses impair vision. The inventive films maintain surfaces clean of organic contaminants. Inorganic, non-oxidizable contaminants are readily removed by being blown or washed off, once the organic matter that makes them stick to the glass surface is oxidized.

5                   The most preferred method for preparing photocatalytic glass is by acid etching the glass followed by application of the photocatalyst composition and then calcination.

### **Photocatalytic Film**

10                   The photocatalytic film coated glasses of the invention, e.g. containing photocatalytic particles and adherent to glass, are optically clear. They may have a tint or color, but do not absorb or scatter visible light so as to impair visibility through the glass or cause severe glare. The photocatalytic films also adhere to glass and resist abrasion. An inventive film adhering to glass cannot be removed by pressing adhesive tape against  
15 it, as discussed below in Example 1, and rapidly pulling on it (Tape Test). An abrasion resistant film of the invention is not damaged when cleaned with wet or dry paper or cloth, and it typically is not scribed by a pencil of H2 hardness or softer. In general, the photocatalytic film is formed of photocatalytic particles, e.g., TiO<sub>2</sub>, cast onto acid glass and calcined for specific adherence to the glass.

20                   The photocatalyst-containing films of the invention contain a material that, upon exposure to light, particularly UV light, accelerates the oxidation in air of organic compounds absorbed or deposited on the film. One example of such a film is a film containing crystalline, preferably anatase, titanium dioxide. The film is well bound to glass in the present invention, generally through an intermediate barrier layer that prevents  
25 migration of alkali metal oxides, e.g. sodium, yet is transparent to visible light.

### **Glass**

                  The glasses useful in the present invention have varied compositions. The most commercially important and most common glasses comprise sodium and calcium  
30 ions and have a network formed of bonds of silicon and oxygen atoms.

                  The self-cleaning glasses of this invention are usually photocatalytic films cast on common glass, which is formed of silicon dioxide, alkali metal oxides (oxides of

Column I metals of the periodic table), particularly sodium and potassium, and oxides of alkaline earth metals (oxides of Column 2 metals of the periodic table), particularly calcium. In general, the ratio of the number of oxygen atoms to the number of silicon atoms is between 2.2 and 2.7 in the glasses of the invention. In the preferred glasses, the ratio of oxygen atoms to silicon atoms is between 2.2 and 2.5. The glasses may contain other oxides, such as oxides of trivalent or tetravalent rare earths or oxides of aluminum, boron, antimony, germanium, lead and tin. The glasses are transparent, meaning that they can be seen through and are useful as windows, mirrors, windshields, and the like. An example of glass commonly used in such applications and useful in the invention is soda lime glass.

The method of the invention is intended to prevent migration of alkali metal oxides from glass, particularly of sodium and/or potassium, into the precursor of the photocatalytic film and/or into the photocatalyst film by creating a barrier to the migration. When excessive sodium migration is prevented, the photocatalytic film formed upon calcining of its precursor, can efficiently clean its surface of oxidizable contaminants such as carbon-rich organic films.

Glass that is commercially used in windows, mirrors, and optical lenses typically contains significant amounts of alkali metal oxides, such as sodium oxide and potassium oxide (usually at least about 10% by weight). Thus, the methods and coated glasses of the present invention provide for the first time an economically feasible self-cleaning clear glass.

### Photocatalyst

Photocatalysts useful in this invention are generally photoconductors or semiconductors having band gaps greater than 2.5eV and smaller than 4.5eV. The photocatalytic films are generally less than one micron thick, preferably about 40-80 nm thick, and consist of sufficiently small particles to avoid scattering of visible light. Alternatively, the crystallites of the photocatalytic particles are densely packed and oriented so that they do not scatter visible light. The preferred photocatalysts are crystalline oxides, particularly crystalline oxides comprising titanium, tungsten or molybdenum. A particularly useful photocatalyst is titanium dioxide in the anatase phase. Other photocatalysts include  $\text{TiO}_2$  with co-catalysts such as Pt, Pd, Au, Ag, Cu, W, Mo, or

their sulfides and oxides; compound oxides such as  $(\text{SrTiO}_3)$  or  $\text{CaTiO}_3$ , and  $\text{TiO}_2$  in the rutile phase or in the mixed anatase and rutile phases. While a preferred photocatalyst, titanium dioxide, is exemplified herein, it is understood that other photocatalysts, e.g., those described above, forming clear films on glass may also be used.

5 Titanium dioxide in the anatase or the rutile phases has an index of refraction of visible (yellow) light greater than about 2.4. Coating of photocatalyst films on glass having a low refractive index, e.g., soda lime glass which has a refractive index below 1.6, causes an increase in the refractive index. In the specific case of automotive  
10 windshields such an increase can be undesirable, because as the angle between the dashboard and the windshield is reduced or the index of refraction of the windshield is raised, the reflected image of the dashboard becomes visible to the driver looking through the windshield. Such reflection is reduced by forming the photocatalytic film of a combination of the photocatalyst and a material having a lower refractive index than that of the photocatalyst. An example of such a film is one comprising non-crystalline silicon  
15 dioxide ( $\text{SiO}_2$ ) and anatase or rutile  $\text{TiO}_2$ . By way of example, if the film contains up to 90 weight%  $\text{SiO}_2$ , then the index of refraction, in the visible, is only about 1.46. (As compared with 2.4-2.7 in the absence of  $\text{SiO}_2$ .)

#### Photocatalyst Precursor

20 In the present invention, a photocatalyst precursor is generally a film formed of a non-crystalline, three, four, or five-valent element, preferably of an oxide of such an element, which film forms an active photocatalytic film, eg., on calcining in air. The oxide is non-volatile at about  $600^\circ\text{C}$ , and the preferred three, four, or five-valent elements are titanium, tin, tungsten, or molybdenum. Most preferred is  $\text{Ti}^{4+}$ .

25 The photocatalyst-precursor films can be formed by their deposition from a liquid phase, or from a vapor phase. Useful photocatalytic precursor compositions include alkoxides, halides and oxyhalides of titanium, tin, tungsten, or molybdenum, e.g., a titanium tetraalkoxide. A most preferred photocatalyst precursor is a film formed upon partial hydrolysis of titanium tetraalkoxide, followed by polymerization by condensation  
30 of the hydrolysate.

When a photocatalyst-comprising film having a lower refractive index than that of the photocatalyst itself is desired, for example for use in automotive windshields as

described above, the sol of which the photocatalysts precursor film is cast, in addition to the photocatalyst precursor, also contains a precursor of a lower refractive index film. For example, a preferred second component or precursor sol is a precursor of silicon dioxide, e.g., formed by co-hydrolyzing a silicon alkoxide, such as a silicon tetraalkoxide silicon, alkyltrialkoxide or dialkyldialkoxide, co-dissolved with titanium alkoxide acetylacetonate. The ratio of the amounts of the silicon and titanium oxide precursors in the sol are adjusted as needed to obtain the desired refractive index. The photocatalytic film compositions range from pure titanium dioxide to compositions having a 1:10 titanium dioxide:silicon dioxide molar ratio. Preferred low-refractive index films comprise vitreous silicon dioxide and crystalline titanium dioxide phases.

### **Barrier Layer**

In the present invention, a barrier layer is defined as a barrier that slows or stops the diffusion or migration of alkali metal ions (e.g., sodium ions) and/or alkali metal oxides (e.g., sodium oxide) into the photocatalyst precursor film or into the photocatalyst film. The barrier layer operates at the temperatures that the inventive photocatalyst precursor and photocatalyst films experience, and for the duration of the films.

In general, the barrier of the invention is the product of the reaction between hydrogen glass and a photocatalyst precursor as defined above. In the barrier, the most preferred three, four, or five-valent elements are  $\text{Ti}^{4+}$ ,  $\text{Zr}^{4+}$ ,  $\text{Ge}^{4+}$ ,  $\text{Sn}^{4+}$ , and  $\text{Si}^{4+}$ . The most preferred barrier film is the reaction product between acid glass and the precursor of  $\text{TiO}_2$ , and includes the elements silicon, titanium, and oxygen.

### **Forming Photocatalyst Coating on Glass**

A photocatalyst containing layer can be formed on the surface of the glass from a vapor phase or from a precursor dissolved or dispersed in a liquid. The preferred liquids containing the precursor are long lived sols. An example of these is described in Example 1. Stable sols can be formed, for example, of titanium tetraalkoxides, by reacting these first with acetylacetone, then with water. The sols contain polymers of the precursor species or crystallites of the photocatalyst that do not have a longest dimension greater than about 30nm and most preferably not greater than about 20 nm, and are preferably smaller than about 5nm in their larger dimension. The preferred liquid phase in which the

sol is dissolved or dispersed comprises alcohol in excess. Alcohols such as n-propanol, methanol, and butanol are useable.

5 A film of this liquid is applied to the glass surface, preferably to acid or etched glass, formed by acid etching (boiling in 9M sulfuric acid). The volume applied and the concentration of the precursor are selected so that the final thickness of the photocatalyst-containing layer will not be less than 10nm nor more than 500nm. The preferred final thickness is 20-200nm. The film can be formed by known methods, such as spraying microdroplets while the glass is cold or hot; dipping the glass in the liquid then removing it; pouring the liquid onto the glass and leveling the liquid layer  
10 mechanically or by spinning.

The film can also be formed by other methods, including a dry process, such as sputtering or evaporating a metal and then oxidizing it; or by reacting a low molecular weight molecular or metallic precursor in the gas phase prior to its deposition on the glass. For example, a titanium tetraalkoxide can be evaporated and decomposed  
15 either en route to or on the surface of the glass.  $\text{TiCl}_4$  can be reacted with water to form  $\text{TiO}_2$  en route to the surface. In addition, metallic Ti can be reactively sputtered in an  $\text{O}_2$  containing atmosphere to form a  $\text{TiO}_2$  film.

In contrast to prior attempts at coating common glass, relatively active photocatalytically self-cleaning films are formed on common window glass (soda lime  
20 glass) when the glass surface has been treated with a reactant that produces a hydrogen-containing acid glass by exchanging sodium ions with protons and/or by hydrolysis of Si-O-Si bonds, both of which may occur upon acid etching. When materials such as sodium oxide in the glass diffuse into part of the photocatalytic film layer near the glass, phases other than the desired crystalline photocatalyst phase form, and the desired  
25 crystalline phase can become excessively sodium-contaminated. As a result, some of the photoactivity of the film is lost. Reactants that are useful in exchanging sodium ions or other alkali metal ions of the glass at or near its surface (by protons) and thus increase the photocatalytic activity of the coated glass, are generally acids. When the acid glass reacts with a precursor of the crystalline  $\text{TiO}_2$ ,  $\text{ZrO}_2$  or  $\text{SiO}_2$  film, a sodium migration reducing  
30 barrier layer is formed. Even in the presence of this barrier layer, some photoactivity of the crystalline titanium dioxide-comprising films on glass is still lost when sodium oxide

from the glass diffuses into part of the titanium dioxide layer near the glass. Photoactivity can be partially restored by subsequent acid treatment.

#### Acid Etching Glass-Pretreatment

- 5 Etching is the process whereby the reactive acid glass is formed. Chemically, etching may involve one or both of the following processes: Exchange of alkali metal (e.g., sodium) ions of the glass with protons; and scission, through hydrolysis, of Si-O-Si bonds. In both processes, a glass having SiOH junctions is produced. An example of an etchant is boiling 9M aqueous sulfuric acid. This is the preferred etchant.
- 10 In a preferred process of making the photoactive film on glass, the glass is first exposed to acid so that sodium ions are extracted from its surface, being exchanged by protons and thereby forming an acid glass with silicon-bound OH-groups. The treatment with acid can be at ambient or, preferably, at higher temperatures, e.g., at the boiling temperatures of the acid. The glass surface can be rinsed following exposure to
- 15 the acid with water, preferably deionized water, so as to remove any water soluble sodium salt. It has been noticed that treating of the glass with an acid prior to applying the photocatalytic coating to the glass leads to a higher photoefficiency. If the rinsing step is performed, the rinsing solution can be deionized water, or it can also contain a volatile base or ion such as ammonium hydroxide or an ammonium salt.
- 20 Preferred acids for etching glass include those which form a hydrogen glass upon reaction with the glass. An example of such an acid is 9M (50%) sulfuric acid. Most preferably, the glass is reacted with boiling 9M  $\text{H}_2\text{SO}_4$ .

- The photocatalyst precursor or photocatalyst containing film is then deposited on the acid-treated surface. The acid treated glass should not be calcined prior
- 25 to application of the catalytic film, as such calcining lowers the photocatalytic activity. It is suggested that reaction between the acid-treated glass and the photocatalyst crystalline precursor establishes a sodium-migration barrier at the interface of the glass and the film.

#### Photocatalyst Coating

- 30 The acid-treated and optionally rinsed glass is coated with the photocatalyst precursor. When coating is with a liquid, it is preferred that the precursor be in the form of a sol having an ambient temperature shelf life longer than a day. The sol

can be formed, for example, from a titanium tetraalkoxide, such as titanium tetraisopropoxide. The tetraalkoxide is first reacted in an alcohol solution, preferably in an excess alcohol, and preferably in an alcohol solution where the alcohol differs from the one that is evolved from the tetraalkoxide upon its hydrolysis. Although the sol can be formed by adding water to the titanium tetraalkoxide solution, in the preferred process the titanium tetraalkoxide is first reacted with a bifunctional  $Ti^{4+}$  complexing agent, such as acetylacetonate, to form a complex where the titanium to acetylacetonate ratio is 1:1. This complex is then hydrolyzed, preferably at room temperature, by adding water (preferably dissolved in alcohol), preferably at a molar ratio of 10 moles of water per 1 mole of titanium. The resulting precursor sol is generally stable, meaning that when stored for at least a day at a temperature between 5°C and 35°C the solution remains substantially clear.

A uniform film of the photocatalyst-containing compounds is cast on the glass through a process such as spinning, dipping, painting, spraying or applying an excess of solution then spreading it with a blade. The cast film is then allowed to dry.

#### Calcination

The dried-film coated-glass is next calcined, e.g., heated at a temperature to form photocatalytic crystallites and cause the photocatalyst layer to adhere to the glass. Calcination is preferably by heating in air at a rate resulting in a temperature increase of 50°C per minute, then holding at the desired calcining temperature, preferably for about 15 to 30 minutes. The coated glass is then cooled. At this point, this glass is photocatalytically self-cleaning within the scope of the invention.

The calcination temperature is generally in excess of 275°C and less than 650°C, and preferably is in the range of 400°C - 650°C. For calcining films on glass, the most preferred temperature is in the range of 400-550°C; for films on silica, the most preferred range is 550-600°C.

#### Acid Wash - Post Treatment

The photocatalytic activity (i.e. the rate at which the glass cleans itself of an organic contaminant) of the already photocatalyst-coated glass can be further increased by a second treatment, termed "post-treatment", with acid. Post-treatment, even in the

absence of initial acid etching to form the acid glass, increases the low photocatalytic activity, though only to a lesser level than that observed when the glass was acid etched prior to deposition of the photocatalyst precursor. Applicants have found that multiple acid treatments can increase the self-cleaning glass's photoefficiency.

5           In this second, acid wash, post treatment step, the photocatalytic-film-coated glass is again exposed to an acid that reacts with or neutralizes sodium oxide or calcium oxide or a product of these. The preferred acids for this process step are strong mineral acids, the ions of which do not form strong complexes with four valent ions such as titanium ions ( $Ti^{4+}$ ). Dilute aqueous nitric acid, and particularly nitric acid of 0.1M to  
10       3M concentration, with a preferred concentration of 0.2M is useful for this process step. Other useful acids include tetra fluoboric acid and dilute perchloric acid. Examples of acids that are not useful are 6M aqueous hydrochloric acid and 6M aqueous sulfuric acid, both of which dissolve or damage the photocatalytic titanium dioxide film on the glass. In the final process stage the glass may be rinsed, preferably with water, then dried.

15

#### Properties of Self-Cleaning Glass

The inventive self cleaning glasses include a substrate glass, barrier and a photocatalyst, as described above.

20           Self-cleaning glasses of the invention prepared as described above have coatings that strongly adhere to the glass and are abrasion resistant. These self-cleaning glasses have a photoefficiency, as defined in Example 1, when a film stearic acid is photoreacted, of at least  $3.5 \times 10^{-3}$ . In more general terms, the glasses of the invention have a photooxidation rate sufficient to oxidize daily, in direct sunlight, organic  
25       contaminant films at a rate of 50 nm per day or more. At this rate, impaired vision due to a dirty windshield or lens of an eyeglass is minimized. 50 nm thick spots of contaminants interfere with vision, for example, by scattering light and causing glare. The glasses of the invention, as discussed more fully in Example 1, can also withstand successive applications and removals of scotch tape on their coated surfaces (tape test). Glasses of the invention can withstand being scribed with pencils of hardness H2 or softer as  
30       described in Example 1.

## EXAMPLES

The invention may be further understood by reference to the following examples, which are not intended to limit the scope of the invention in any way.

5

### **Example 1** **Preparation of clear photoactive films of titanium dioxide** **on fused silica slides by spin coating**

Clear, approximately 60 nm thick films of titania were produced on fused silica by a sol-gel process. The sol was made of a precursor solution prepared by mixing 4.5 mL  $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ , (97% in propanol) with 10.0 mL n-propanol and 1.6 mL acetylacetone (acac) to provide a stock solution having Ti:propanol:acac molar ratio of about 1:9:1.05. After aging for a week at room temperature (about 20°C - 25°C), a casting solution was prepared by mixing 1.0 ml of the precursor solution with a 1.8 ml water/n-propanol solution (1:9 v/v), the resulting water to titanium ratio being about 11:1. A clear, yellow casting solution, stable for at least two months and having a viscosity of 2.3 cp was obtained. Viscosity was measured using a falling ball type viscometer.

Prior to casting, the fused silica slides were rinsed in a cleaning solution (usually methanol), washed thoroughly with de-ionized water, and dried in a stream of air. The casting solution was then spread on the substrate (0.03 mL per 2.5x2.5 cm slide) which was spun, after the application, for 2 minutes at 4000 rpm to dryness. In the next stage, the coated silica slides were heated in air to 500°C at a rate of 50°C min<sup>-1</sup> and were calcined at this temperature for 30 minutes. The calcination transformed the product of the hydrolytic reaction into a microcrystalline oxide, stripped all organic residues, and bound the  $\text{TiO}_2$  film to the substrate. Multiple  $\text{TiO}_2$  layers were produced by applying a layer, drying in an oven (90°C, 10 minutes), applying another layer and finally calcining.

The process yielded uniform, clear and non-scattering films, as measured with a HP 8452A spectrometer (Figure 1). Comparison with the UV absorption spectrum of "milky" film coatings made of larger particles (Degussa P-25) revealed that the absorption edge of the clear films was shifted by 30-40 nm to the blue, as expected for nanoparticles in which electrons are confined.

The thickness of the films, 60±15 nm for a one layer film, was determined with an Alpha step 200 profilometer (Tencor Instruments). Transmission

electron diffraction patterns and images of the thin films were obtained using JEOL-1200EX and JEOL-2010 microscopes. For these measurements, the films were detached from their supports by pressing 200 mesh copper grids against the films while boiling in potassium hydroxide solution (6 M), following by thorough washing of the grids with water to remove any potassium residues. The electron diffraction ring patterns obtained by this method were indexed as that of  $\text{TiO}_2$  in the anatase phase and the dark field imaging suggested that the crystallites were segmented, with a typical segment being approximately 3 nm in diameter.

The resultant films were not damaged when wiped aggressively with any of several types of paper, including "Kimwipe", office copying machine paper, and newsprint, whether dry or wet. Furthermore, the films could not be removed by 20 successive applications and removals of Scotch® adhesive tape (3M-810), nor damaged when scribed with pencils of hardness H2 or softer.

The photoactivity of the various coated slides was tested by casting thin films of stearic acid ( $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ ) on the  $\text{TiO}_2$ -coated substrates and measuring at a defined irradiance the rate of decrease in the integrated absorbance of the ensemble of the C-H stretching vibrations between  $2700\text{ cm}^{-1}$  and  $3000\text{ cm}^{-1}$ .

The measurements were performed on batches of 8-12 slides. The organic films were cast by applying  $3 \times 10^{-2}$  ml of  $8.8 \times 10^{-3}$  M stearic acid in methanol per slide and spinning at 1000 rpm for 2 minutes to dryness. The integrated IR absorbance of the stearic acid films was measured by a Nicolet Magna IR-750 FTIR. The actual number of stearic acid molecules on the surface was calculated based on the integrated absorbance of densely packed monolayers of homologs having a known area per molecule (such as octadecyl trichlorosilane, arachidic acid and behenic acid). A typical stearic acid film had, prior to illumination, an integrated absorbance of  $0.6\text{ cm}^{-1}$  corresponding to  $\sim 1.9 \times 10^{15}$  molecules  $\text{cm}^{-2}$ .

The UV light source for the photoefficiency measurements was either a UVA wide band lamp, the peak emission being at 365 nm (Hideaway 6000 Solarium, Helitron Ltd.) or a 254 nm line-emitting mercury lamp (Sylvania G30T3). The irradiance, measured at the slide surface, was  $2.4 \pm 0.4\text{ mW cm}^{-2}$  for the UVA source and  $0.8 \pm 0.15\text{ mW cm}^{-2}$  for the 254 nm source, corresponding to respective fluxes of

4.4x10<sup>15</sup> photons sec<sup>-1</sup> cm<sup>-2</sup> and 1.0x10<sup>15</sup> photons sec<sup>-1</sup> cm<sup>-2</sup>. These fluxes resulted in photocarrier generation rates differing only by a factor of 1.3, because of the large fraction of 254 nm UV photons absorbed in the 60 nm thick films in comparison to the lower fraction absorbed at the longer wavelength. The values given for the irradiance are the average between the readout of a JBA100 power meter and a second measurement by a well known photochemical method, potassium ferrioxalate actinometry.

Within the context of this application, the photoefficiency is defined as the number of carbon - hydrogen bonds of stearic acid stripped from the photocatalyst surface per incident photon,  $dA \times K \times N / f$ , where  $dA$  is the change in the integrated IR absorbance of the C-H vibrations of the stearic acid per minute;  $K$  is the number of C-H bonds in a stearic acid molecule (35);  $N$  is the number of stearic acid molecules per cm<sup>2</sup> per integrated absorbance unit, having a value of  $3.17 \times 10^{15}$ ; and  $f$  is the irradiance ( $2.6 \times 10^{17}$  photons cm<sup>-2</sup> minute<sup>-1</sup> for the UVA source and  $6 \times 10^{16}$  photons cm<sup>-2</sup> minute<sup>-1</sup> for the mercury lamp).

The integrated absorbance of the organic contaminant's infrared C-H stretching vibrations was measured as a function of the exposure time. Figure 2 presents the FTIR spectra of a TiO<sub>2</sub> film on silica contaminated with stearic acid prior to and after exposure to the UVA light for 7.5 minutes. In general, the rate at which the stearic acid film was stripped remained constant during the exposure, as long as a continuous stearic acid film remained on the surface of the photocatalyst. Thus, the efficiency of the photoreaction was generally independent of time, remaining constant throughout the reaction period. Table 1 presents the integrated absorbance of stearic acid on silica coated with the photoactive TiO<sub>2</sub> films following illumination with the UVA light. The efficiency in the table was calculated based on the change following 7.5 minutes of illumination.

The photoefficiency of a fused silica substrate coated with a single layer of TiO<sub>2</sub> film was between  $14 \times 10^{-3}$  and  $21 \times 10^{-3}$  upon illumination with the UVA light and between  $45 \times 10^{-3}$  and  $81 \times 10^{-3}$  upon illumination with the 254 nm light, the ratio between efficiencies being scaled with the ratio in the number of photons absorbed per

cm<sup>2</sup> per second at each wavelength. Values, averaged over more than 25 slides are presented in table 2.

**Table 1**

Slide No.	No. of TiO <sub>2</sub> layers	Integrated absorbance t=0	Integrated absorbance t=3.75 min.	Integrated absorbance t=7.5 min.	Integrated absorbance t=15 min.	efficiency
65	1	0.88		0.55	0.31	$18.8 \times 10^{-3}$
205	1	0.63	0.51	0.35	0.2	$15.9 \times 10^{-3}$
206	2	0.78	0.60	0.45	0.2	$18.8 \times 10^{-3}$
247	2	0.89	0.70	0.58	0.24	$17.6 \times 10^{-3}$
249	2	0.85	0.70	0.57	0.25	$15.9 \times 10^{-3}$

**Table 1:** Changes in the integrated absorbance of the FTIR C-H stretch band of stearic acid on silica slides coated with clear and photoactive TiO<sub>2</sub> upon illumination with UVA light. The efficiency given in the table was calculated based on the change after 7.5 minutes of exposure.

**Table 2**

	Glass substrate		Silica substrate	
	365 nm	254 nm	365 nm	254 nm
TiO <sub>2</sub> (clear) on non-etched substrate	$(0.7 \pm 0.35) \times 10^{-3}$	$(17.5 \pm 3.5) \times 10^{-3}$	$(17.5 \pm 3.5) \times 10^{-3}$	$(63 \pm 17.5) \times 10^{-3}$
TiO <sub>2</sub> (clear) on etched substrate	$(9.1 \pm 2.8) \times 10^{-3}$	$(58 \pm 18) \times 10^{-3}$	$(21 \pm 3.5) \times 10^{-3}$	$(73.5 \pm 28) \times 10^{-3}$

**Table 2:** Photoefficiency (number of C-H bonds consumed per impinging photon) of TiO<sub>2</sub> clear films on glass and on fused silica substrates, showing the effect of H<sub>2</sub>SO<sub>4</sub> etching of the substrate upon the efficiency. The values are averages for 20-30 samples.

**Example 2**  
**Preparation of clear photoactive films of titanium dioxide**  
**on soda lime glass slides by spin coating**

5 Clear, photoactive films of titanium dioxide were produced on soda lime glass (Corning 2947, composed of O (60 atom%), Si(24.5 atom%), Na(10 atom%), Ca(2.5 atom%), Mg(2 atom%), and Al(1 atom%) by the sol-gel method described for Example 1. In the first step of their preparation, the substrates were cleaned by an organic solvent (usually methanol or chloroform), then etched by boiling them for at least 30 minutes in fuming 50% (9M) sulfuric acid at 240°C. After being cooled to ambient temperature, the slides were washed with de-ionized water and dried in a stream of air. Then, the same organotitanate coating solution described in Example 1 was applied onto the surface (0.04 ml per 3.75x2.5x1 mm slide) which was spun, as described for Example 1. The coated glass substrates, were calcined usually at a temperature of 400 °C, thus producing clear and homogeneous films, denoted as GE films. For comparison, TiO<sub>2</sub> films on non-etched glass slides, denoted as GN, and TiO<sub>2</sub> films on etched and on non-etched silica (denoted SE, SN respectively) were produced in the same manner. Thicker films were produced either by applying a first layer of the titanate precursor solution, oven drying (90 °C, 10 minutes), applying a second layer and calcination or by repeating the single layer preparation process. The former class is denoted as (2), whereas the latter is denoted as (1+1).

All films, whether GE, GN, SE, or SN withstood the abrasion tests described in Example 1. A ratio of BET (Brunauer-Emmett-Teller) to geometrical surface area of approximately 20 was determined for the TiO<sub>2</sub> coated glass slides by N<sub>2</sub> BET adsorption isotherms, using a Micromeritics AccuSorb system. Characterization of the films, i.e. UV, TEM and profilometry measurements were performed as described in Example 1. Figure 2 shows the UV absorption spectra of clear TiO<sub>2</sub> films on etched glass (dashed line) and on non-etched glass (solid line), the latter being blue shifted by 4-5 nm with respect to the former. As seen below, the difference between the spectra of films on etched glass (GN type) may have resulted of the GN type films not having the anatase phase or of smaller crystalline domains in the GN type films. "Plan view" TEM images of the TiO<sub>2</sub> films, detached from their substrates in the same manner as described in Example 1, revealed a distinct difference between type GE and type GN

films. Type GE films were found to be identical to the SN films described in Example 1 (i.e. consisted of segmented nanocrystallites having the anatase phase) whereas the type GN films were typical for materials having no long range order, with a diffused ring in their selected area diffraction pattern corresponding to an interplanar distance of 2.6 -3.6 Å.

The compositions of the supported films, as well as of the glass substrates, were measured by x-ray photoelectron spectroscopy (VG-ESCALAB). To obtain depth profiles, the samples were sputtered with an argon gun (Varian 981-2043, 3 kV, 25 mA) and re-measured. The estimated sputtering rate was 0.15 nm min.<sup>-1</sup>. For these measurements, the samples were cut into 8 mm x 8 mm slides, that were attached to their pedestals by a conducting adhesive tape to reduce charging during the sputtering process.

Table 3 presents the percentage of sodium atoms in various TiO<sub>2</sub> clear films on soda lime glass, and in glass slides, some pre-etched, some non-etched and some calcined after being etched, as deduced from the XPS measurements. These values are based on the area of the sodium and oxygen 1S peaks taking sensitivity factors (sf) of 2.51 and 0.63, respectively, and on the area of the 2P doublet (2P<sub>3/2</sub> + 2P<sub>1/2</sub>) peak of titanium, taking a sensitivity factor of 1.59. Whenever silicon was found, for example in the glass samples or after prolonged sputtering of the TiO<sub>2</sub> samples, its atomic fraction was calculated from its 2P peak (sf=0.17). No constituents apart from titanium, oxygen, and sodium were found in the TiO<sub>2</sub> films.

**Table 3**

Pre-treatment	Sputtering time (min.)	glass		TiO <sub>2</sub> on glass (one layer)		TiO <sub>2</sub> on glass (two layers)	
		Not calcined	calcined	untreated	HNO <sub>3</sub> treated	untreated	HNO <sub>3</sub> treated
Non-etched	0	7.2	35.0	21.5	2.0	14.0	2.5
	30						
	60			13.6			
	90	9.1	12.8		2.5		
	180	3.4	8.7	14.5			
	300	5.3		14.1			
	420			17.1	18.0		
Etched	0	1.8	7.5	8.4	3.2	7.7	0.0
	30	0.5			1.1		
	60			7.0			
	90		3.4				
	120			4.4			0.0
	150				1.6		
	300			3.0			

Atomic percentage (%) of sodium measured by XPS, in soda lime glass and in clear films of TiO<sub>2</sub> on soda lime glass.

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A high atomic fraction of sodium was measured not only at the interface between the TiO<sub>2</sub> and the glass but also at the air interface. The concentration of sodium at the air interface was actually higher than in the bulk of the films. Evidently, the sodium diffusion length exceeded the film thickness and sodium segregated at the surface of the titanium dioxide film. The effect of etching the glass prior to coating with the TiO<sub>2</sub> precursor on the sodium concentration at the TiO<sub>2</sub> film surface is evident, the atomic percentage of sodium in the GE films being 2-3 times lower than that in the GN films. In the GN films the atomic percentage of sodium exceeded that in the bulk of the soda lime glass (10 atom%), showing that the film was not only contaminated with sodium, but actually extracted sodium from the glass. The amount of sodium in the thicker photocatalyst films made by applying two layers of the organo-titanate precursor and then calcining, was only slightly smaller than in films made of one layer. A high atomic percentage (7.5%) of sodium was found on the glass surface after it was etched and calcined. Nevertheless, the fraction of sodium at the surface of the non-etched but calcined glass was far higher (35%). Thus, the pre-etching of the glass prior to application and calcining the photocatalyst precursor film caused effective blocking of sodium migration into the photocatalyst film.

20

The photoefficiency of the photocatalytic stearic acid stripping process, as defined in Example 1, was between  $5 \times 10^{-3}$  and  $12 \times 10^{-3}$  for the GE slides illuminated with the UVA light whereas for the  $\text{TiO}_2$  films made on non-etched glass (the GN films) it was at least 7 times less. The photoefficiency results obtained for a batch containing 12 slides, half of which were GE type while the other half were GN type are given as an example in Table 4. In Table 2 the average photoefficiencies obtained for  $\text{TiO}_2$  clear films on fused silica, on glass etched by  $\text{H}_2\text{SO}_4$  prior to coating with the titanium precursor, and on non-treated glass are presented. Each value listed in the table represents an average for more than 25 samples. For soda lime glass substrates, a large difference in the photoactivity was found between GE type and GN type samples, the latter being several times less efficient than the former. This difference was greater for excitation upon 365 nm photons than by 254 nm photons. In contrast to the observed difference in efficiency between films on etched and on non-etched glass, etching did not increase or reduce the photoactivity when the films were coated on fused silica.

TABLE 4

Slide No.	Pre-treatment	Photoefficiency (%)
398	50% $\text{H}_2\text{SO}_4$ (boiled), 30 min.	$4.9 \times 10^{-3}$
399	50% $\text{H}_2\text{SO}_4$ (boiled), 30 min.	$5.25 \times 10^{-3}$
400	50% $\text{H}_2\text{SO}_4$ (boiled), 30 min.	$8.4 \times 10^{-3}$
401	50% $\text{H}_2\text{SO}_4$ (boiled), 30 min.	$8.05 \times 10^{-3}$
402	50% $\text{H}_2\text{SO}_4$ (boiled), 30 min.	$7.7 \times 10^{-3}$
403	50% $\text{H}_2\text{SO}_4$ (boiled), 30 min.	$8.05 \times 10^{-3}$
404	without pre-treatment	$.35 \times 10^{-3}$
405	without pre-treatment	$.7 \times 10^{-3}$
406	without pre-treatment	$.7 \times 10^{-3}$
407	without pre-treatment	$.35 \times 10^{-3}$
408	without pre-treatment	$.35 \times 10^{-3}$
409	without pre-treatment	0.0
410	without pre-treatment	$.7 \times 10^{-3}$

The dependence of the efficiency of clear films of titanium dioxide on the calcination temperature is seen in Figure 4. In etched glass type (GE) films on soda lime glass, the efficiency decreased when the calcination temperature exceeded 450°C (B,C), whereas on fused silica no decrease in efficiency was observed at higher calcination temperatures (A). The absence of loss of efficiency in silica-supported films indicated that the cause of loss in the photoactivity was not sintering, leading to lower surface area. The results obtained with 254 nm light were similar, but the decrease in photoactivity of TiO<sub>2</sub> on soda lime glass upon calcination at elevated temperatures was less pronounced.

The effect of the duration of the etching in sulfuric acid at 240°C on the 365 and 254 nm photoefficiencies is seen in Figure 5. While etching for 10 minutes sufficed to produce a film which was highly photoactive under 254 nm light (filled circles), more than 45 minutes of etching were needed for best activity under 365 nm light (open circles).

Table 5

Batch number and (# of samples)	Film Type and wave-length	As is	Double calcination	NaNO <sub>3</sub> treatment	NaNO <sub>3</sub> treatment + calcination	NaOH soaking	NaOH soaking + calcination
1 (2)	P-25, 365 nm Degussa	55.3 x 10 <sup>-3</sup>	40.6 x 10 <sup>-3</sup>	40.95 x 10 <sup>-3</sup>	9.45 x 10 <sup>-3</sup>	4.2 x 10 <sup>-3b</sup>	6.3 x 10 <sup>-3b</sup>
2 (2)	P-25, 254 nm Degussa	92.75x10 <sup>-3</sup>	-	136.85x10 <sup>-3a</sup>	33.6 x 10 <sup>-3a</sup>	75.6 x 10 <sup>-3b</sup>	10.15x10 <sup>-3b</sup>
3 (2)	Etch glass, 4 layers, 365 nm.	14 x 10 <sup>-3</sup>	14.35x10 <sup>-3</sup>	6.3 x 10 <sup>-3a</sup>	0.35 x 10 <sup>-3a</sup>	0 <sup>b</sup>	0 <sup>b</sup>
4 (2)	Etch glass, 4 layers, 365 nm.	12.25x10 <sup>-3c</sup>	13.65x10 <sup>-3c</sup>	9.1 x 10 <sup>-3a,c</sup>	2.8 x 10 <sup>-3a,c</sup>	10.85 x 10 <sup>-3</sup> <sub>b,c</sub>	0 <sup>b,c</sup>
5 (1)	Etch glass, 4 layers, 365 nm.	16.45 x 10 <sup>-3</sup>	12.6 x 10 <sup>-3</sup>	17.6 x 10 <sup>-3d</sup>	07.35 x 10 <sup>-3d</sup> 12.95 x 10 <sup>-3d,e</sup>	-	-
6,7 (4)	Etch glass, 7 layers, 365 nm.	18.2x10 <sup>-3</sup>	-	-	11.2 x 10 <sup>-3f</sup>	-	11.2x10 <sup>-3g</sup>

Table 5: Photoefficiency of TiO<sub>2</sub> films, expressed as the number of C-H bonds in a steric acid film consumed per impinging photon.

a-Dipping in NaNO<sub>3</sub> (1 M, 10 minutes, 20°C).

b-Dipping in NaOH (1 M, 10 minutes, 20°C).

c-Batch 4 obtained by washing batch 3 slides with methanol to remove stearic acid residues, immersion in water and drying.

d-Dipping in  $\text{NaNO}_3$  (0.2 M, 10 minutes,  $20^\circ\text{C}$ ).

e-Washing after calcination.

f-3 layers of  $\text{TiO}_2$ , calcination,  $\text{NaNO}_3$  layer by spin coating (0.2 M, 1250 rpm, 1 minute), calcination, washing and coating with 4 additional layers of  $\text{TiO}_2$ .

5 g-3 layers of  $\text{TiO}_2$ , calcination,  $\text{NaNO}_3$  layer by spin coating (0.2 M, 1250 rpm, 1 minute), calcination, washing and coating with 4 additional layers of  $\text{TiO}_2$ .

Table 5 demonstrates the deleterious effect of sodium contamination on the efficiency of titanium dioxide films on glass. Dipping of the clear  $\text{TiO}_2$  films in  
10  $\text{NaOH}$  (1M,  $20^\circ\text{C}$ ) reduced their efficiency under 365 nm light to nil (Table 5, batch 3), and subsequent washing with de-ionized water led to recovery of the efficiency (Table 5, batch 4). However, when the  $\text{NaOH}$  treated slides were calcined, the loss of their efficiency could not be reversed (Table 5, batches 3,4). Double calcination of GE films (Table 5, batches 3-5) did not increase or decrease their efficiency. Films made of  
15 Degussa P-25 that were immersed in  $\text{NaOH}$  were 10 fold less efficient than untreated films, under 365 nm light (Table 5, batch 1). Immersion of P-25 samples in  $\text{NaOH}$  had, however, a less severe effect on their photoactivity at 254 nm (Table 5, batch 2). Untreated P-25 films showed a moderate decrease in efficiency upon a second calcination (Table 5, batch1), possibly because their surface area was reduced.

20 Etched glass type (GE) films did not show a significant loss in photoefficiency at 365 nm after immersion in a 0.2M  $\text{NaNO}_3$  solution (Table 5, batches 3-5). Dipping in  $>1\text{M}$   $\text{NaNO}_3$  reduced, however, the 365 nm efficiency by  $\sim 50\%$ . The efficiency of films made of P-25 was reduced by dipping in 1M  $\text{NaNO}_3$  by 25% at 365 nm (Table 5, batch 1). No loss in efficiency was observed for 254 nm light (Table 5,  
25 batch 2). Films calcined following their immersion in  $\text{NaNO}_3$  had only 10-40% of the efficiency of untreated films under 365 nm light (Table 5, batches 3-5). The efficiency of the P-25 films subjected to the same treatment was only 20% of the efficiency of untreated films under UVA light (Table 5, batch 1), and 40% under 254 nm light (Table 5, batch 2). Washing with water after the calcination of  $\text{NaNO}_3$  treated GE films  
30 increased the efficiency of the calcined samples, probably by removing some of the sodium ions on the surface (Table 5, batch 4). In a sandwiched structure, where a  $\text{NaNO}_3$  layer, decomposing upon calcination to  $\text{Na}_2\text{O}$ , was introduced on a calcined  $\text{TiO}_2$  film made of 3 precursor layers, then covered with 4 layers of  $\text{TiO}_2$  precursor and

calcined, the efficiency was only 60% of the efficiency of clear films made of 7 precursor layers without  $\text{NaNO}_3$  (Table 5, batch 5).

To probe the effect of a second calcination, two batches of slides was prepared. In one the first precursor layer was applied to the etched glass, oven dried (90  
5 oC, 10 min.), coated with a second layer, then calcined. These slides were termed GE(2). The second batch was made by repeated coating and calcination of an etched glass slide. These slides were termed GE(1+1). The absorption spectra of the two batches were identical, showing that the sizes of the crystallites, their phases and the thickness of the films did not differ. The GE(1+1) films, despite being calcinated twice,  
10 did not show lesser photoactivity than the GE(2) films. When the glass was etched, then calcined (GC type samples) and then overcoated with the  $\text{TiO}_2$  precursor and re-calcined the efficiency was only 20-40% of that of the standard 1 layer GE film.

The XPS results show that sodium migrates from the soda lime glass substrate into the titanium dioxide layer during the calcination step. When the sodium  
15 was extracted from the surface of the soda lime glass, and when the extracted glass was overcoated with the organo-titanate precursor and calcined, then the sodium content in the titania films was significantly lower. Such lowering affected the titanium containing phase that formed and thereby the photocatalytic behavior. It is known that at temperatures below 550°C, the extraction of sodium from glass is governed by an ion  
20 exchange mechanism and is limited by the rate of the diffusion of sodium ions rather than by the rate of diffusion of protons. If the process of etching would not introduce a change in the glass structure and if charge neutrality would be maintained only through protonation of the originally sodium occupied sites, i.e. if a "hydrogen glass" would have formed, than calcination at 400°C should have resulted in complete recovery from  
25 the extraction, the  $\text{Na}^+$  being redistributed simply because of the higher  $\text{Na}^+$  diffusion coefficient at the calcination temperature of 400°C relative to that at the extraction temperature of 240°C ( $2 \times 10^{-9} \text{ cm}^2 \text{ sec}^{-1}$  versus  $2 \times 10^{-11} \text{ cm}^2 \text{ sec}^{-1}$  respectively, for a soda lime glass of similar composition). However, if the extraction of sodium and the formation of a "hydrogen glass" were followed by loss of water, then a layer of denser  
30 glass, containing fewer ion exchanging Si-OH functions and less permeable to  $\text{Na}^+$  ions would be formed. Formation of such a layer was proposed for dealkalization of soda

lime glass in atmospheres containing water vapor and SO<sub>2</sub>. Such a sodium diffusion limiting layer is formed in glass by etching and calcination. Despite limiting the sodium diffusion, this layer does not completely prevent the migration of sodium, as is evident from the difference between the atomic percentage of sodium in etched glass prior to  
5 (1.8%) and after (7.5%) calcination. The results show that the atomic percentage of sodium in the surface layer of soda lime glass that was etched and then calcined was much smaller than in glass calcined without being etched (7.5% vs. 35% at the surface, and 3.4% vs. 12.8% after 90 minutes of argon sputter etching).

Depth profile measurements show a constant concentration of sodium  
10 across the TiO<sub>2</sub> film in both GE type and GN type films, with an increase in the sodium concentration at the air interface. Apparently, the nanocrystalline TiO<sub>2</sub> film has a greater affinity for sodium than the silicate network of soda lime glass, particularly when the surface of the crystallites is hydrated and the protons are sodium exchangeable, H<sub>2</sub>Ti<sub>n</sub>O<sub>2n+1</sub> being a stronger acid than H<sub>2</sub>Si<sub>n</sub>O<sub>2n+1</sub>. In silicate  
15 glasses, but not necessarily in TiO<sub>2</sub> films on glass, sodium also accumulated at the surface upon hydration of the silicate network, sodium segregation at the surface being coupled with depletion of sodium from the layer below. The sodium depleted layer observed in silicate glasses was not observed in the GE films, showing that Na<sup>+</sup> accumulated throughout the film, not only at its air interface.

20 It was particularly noteworthy that the concentration of sodium in the GN films was higher than in the soda lime glass itself. This higher concentration can be rationalized by Ti-OH being a stronger acid than Si-OH, because of the more electropositive nature of Ti<sup>+4</sup> relative to Si<sup>+4</sup>, combined with fast sodium diffusion across the film.

25 Because the sodium ions were uniformly redistributed by the 400°C calcination step, the ions diffusing rapidly through the nanocrystalline TiO<sub>2</sub> layer, similar sodium concentrations in the "type GE" and the "type GN" films would have been observed, were it not for the existence of a sodium transport limiting layer at the TiO<sub>2</sub> - extracted glass interface. The massive difference between the GE type and GN  
30 type films is explained by creation of a zone in the GE-type films through which sodium permeation was slow. When the precursor temperature is raised nucleation, crystal

growth, and oxidation of organic residues take place. The sodium concentration in the titanium dioxide film was not related to its final concentration at the glass-titania interface, but to its concentration at this interface at the start of the calcination, when the unique sodium diffusion limiting layer was formed. Sodium extraction followed by a first calcination, then by coating with the  $\text{TiO}_2$  precursor and by a final calcination did not provide films as photoactive as those obtained when in the first calcination the  $\text{TiO}_2$  precursor was already present. Therefore, dehydration and compacting of the glass accounted only for part of the sodium transport characteristics of the layer. The unique sodium transport limiting characteristics are explained by reaction of the decomposing anatase  $\text{TiO}_2$  precursor and the dehydrating hydrogen glass, and/or by fast nucleation and growth at the interface between the glass and the  $\text{TiO}_2$  precursor layer.

In the type GN films, in contrast with the type GE films, there was no long range order. Earlier work has shown that titanium dioxide films on non etched soda lime glass were of brookite phase when formed by rapid heating of a film of a hydrolyzed titanium alkoxide precursor ( $>25^\circ\text{C}/\text{min}$ ), and that a  $\text{Na}_2\text{O}\cdot\text{xTiO}_2$  phase was formed when the temperature was raised sufficiently slowly to allow diffusion of the sodium ions from the glass into the  $\text{TiO}_2$  layer. The absorption edge of  $\text{Na}_2\text{O}\cdot\text{xTiO}_2$  was found to be shifted by 10-12 nm to shorter wavelengths relative to the edge of anatase, whereas the absorption edge for the brookite structure was identical with that of anatase. the data did not reveal the existence of well defined phases in the GN films, possibly because a slowly polymerizing chelated precursor was used. Hence, sodium could diffuse into the nascent  $\text{TiO}_2$  film in amounts sufficient to prevent its crystallization.

The photoefficiency invariably decreased when the  $\text{Na}^+$  concentration increased in the  $\text{TiO}_2$  films. Furthermore, the photoactive GE films lost efficiency when soaked in  $\text{NaNO}_3$  and calcined at temperatures where the  $\text{NaNO}_3$  decomposed to sodium oxide. The lesser efficiency of films on soda lime glass relative to films on fused silica presented in Example 1 could have resulted either of the presence of non-anatase phases or the presence of sodium oxide at the air interface, where it would have raised the local pH. In films on non etched glass the sodium fraction exceeded 10 atom% and, as a result, formation of an ordered anatase, brookite or sodium titanate

phase was inhibited. This reduced the efficiency practically to nil for 365 nm illumination. In contrast, on etched glass there were only crystalline anatase domains, even though their sodium atom percentage was as high as 8%.

Because a sodium transport blocking layer forms of the hydrogen glass and the nascent, yet non-crystalline TiO<sub>2</sub> layer, sodium diffusion takes place mainly during the beginning of the calcination process, and a second calcination has only a minor effect on the efficiency of the films (Table 5). That the critical step for prevention of sodium ion migration is the reaction of the hydrogen glass with the nascent TiO<sub>2</sub> layer was also suggested by comparison of the efficiency of films prepared by two methods involving (a) applying a first layer, calcination, then applying a second layer and calcining again and (b) applying two successive layers and calcining only once. There was little or no difference in the photoefficiencies of the two films. The fact that the TiO<sub>2</sub> film made on etched and calcined (GC type) glass had only 20-40% of the efficiency of a TiO<sub>2</sub> film made by coating the precursor on etched but not calcined glass suggests that the sodium transport limiting layer, formed by interdiffusion of TiO<sub>2</sub> and hydrogen glass, was a superior sodium transport blocker to the film formed on the dehydrated hydrogen glass.

Transport of sodium from the substrate into the photocatalyst film precursor and into the photocatalyst films is detrimental to their photocatalytic activity. The TiO<sub>2</sub> films have a higher affinity for sodium ions than the soda lime glass itself and extract the sodium ions from the glass during the calcination step. Sodium transport to the TiO<sub>2</sub> layer can be retarded by forming a blocking layer. Such a layer forms upon calcining the TiO<sub>2</sub> precursor film on the hydrogen glass, formed upon extraction of the sodium with hot acids such as sulfuric acid.

25

### Example 3

#### Preparation of clear photoactive films of titanium dioxide with enhanced photoactivity on soda lime glass

30

Clear films of titanium dioxide were made on soda lime glass either with or without acid pre-treatment (types GE and GN respectively) as described in Example 2. Following their calcination, the samples were post-treated with dilute nitric acid,

usually by soaking them in 0.2 M HNO<sub>3</sub> for 15 minutes at 22 ± 3°C, then washed with water to remove acid residues.

In Table 3 the effect of post-treatment on the atomic percentage of sodium is presented. The atomic percentage of sodium in all films (GE(1), GN(1), GE(2), GN(2) as defined in Example 2) was reduced significantly by the post treatment. For example, from 8.4% to 3.2% at the surface of a titanium dioxide film on etched glass and from 21.5% to 2% at the surface of a TiO<sub>2</sub> film on non-etched glass, manifesting the replacement of sodium ions in the films by protons from the acid.

Table 6 presents the efficiency (as defined in Example 1) measured for a batch of slides containing GN and GE slides, with and without post -treatment, upon illumination with the UVA source. In Table 6, pretreatment means boiling the uncoated glass in 9M sulfuric acid for 30 minutes. "without water wash" means that the slide was dried with a residue of nitric acid. "With water wash" means that any residual nitric acid was removed by washing with de-ionized water. The average efficiencies of slides with a post-treatment versus the average efficiencies without such a treatment are presented in Table 7. In Table 7, "treated with HNO<sub>3</sub>" means soaked in HNO<sub>3</sub> 0.2 M for 15 minutes, followed by a water wash.

**Table 6**

Slide No.	Pre-treatment	Post-treatment	Photoefficiency (%) without water wash	Photoefficiency (%) with water wash
656	yes	yes	14.7 x 10 <sup>-3</sup>	10.15 x 10 <sup>-3</sup>
657	yes	yes	14.0 x 10 <sup>-3</sup>	11.9 x 10 <sup>-3</sup>
658	yes	no	9.1 x 10 <sup>-3</sup>	7.35 x 10 <sup>-3</sup>
659	yes	no	7.0 x 10 <sup>-3</sup>	7.35 x 10 <sup>-3</sup>
662	no	no	1.05 x 10 <sup>-3</sup>	1.05 x 10 <sup>-3</sup>
663	no	no	0.35 x 10 <sup>-3</sup>	0.35 x 10 <sup>-3</sup>
666	no	yes	3.85 x 10 <sup>-3</sup>	2.1 x 10 <sup>-3</sup>
667	no	yes	3.15 x 10 <sup>-3</sup>	1.75 x 10 <sup>-3</sup>

**Table 7**

	365 nm		254 nm	
substrate	non treated	treated with HNO <sub>3</sub>	non treated	treated with HNO <sub>3</sub>
non-etched glass	$0.945 \times 10^{-3}$	$2.31 \times 10^{-3}$	$12.95 \times 10^{-3}$	$17.85 \times 10^{-3}$
etched glass	$8.4 \times 10^{-3}$	$9.8 \times 10^{-3}$	$56 \times 10^{-3}$	$64.4 \times 10^{-3}$

HNO<sub>3</sub> post-treatment significantly increased the photoefficiency of non-etched glass (GN type) TiO<sub>2</sub> films although their photoefficiency remained much smaller than that of the standard etched glass (GE) TiO<sub>2</sub> films. In GE type films the improvement was slighter. Evidently, post-treatment was not an effective substitute for pre-etching of the glass. The gain efficiency upon HNO<sub>3</sub> post treatment was partially lost with time, as observed in repeated measurements. No increase in efficiency was observed upon HNO<sub>3</sub> treatment of films prepared according to Example 1 on fused silica (Table 8), manifesting that the observed increase in efficiency in the TiO<sub>2</sub> coated glass was not due to a lowered surface pH. The cause of the improvement was reaction or neutralization of sodium oxide or its products that migrated to the titanium dioxide layer's surface during the calcination process.

**Table 8**

Slide No.	Slide Type	Post-Treatment	Photoefficiency (%)
a	TiO <sub>2</sub> /quartz	untreated	$14.7 \times 10^{-3}$
b	TiO <sub>2</sub> /quartz	untreated	$11.9 \times 10^{-3}$
c	TiO <sub>2</sub> /quartz	soaking in HNO <sub>3</sub> 0.2 M (22°C, 15 min.)	$12.6 \times 10^{-3}$
d	TiO <sub>2</sub> /quartz	soaking in HNO <sub>3</sub> 0.2 M (22°C, 15 min.)	$10.85 \times 10^{-3}$

For treating titanium dioxide films on soda lime glass, the acid chosen was nitric acid. The anion of this acid, in contrast to with the anions of sulfuric and

hydrochloric acid does not complex the four valent titanium ion. The rate of dissolution of the photoactive film in nitric acid was consequently much slower than its rate of dissolution in sulfuric or hydrochloric acid at the same normalities. Within this context, it is noteworthy that GE films were more resistant to soaking in concentrated acids than the GN films.

Soaking of the  $\text{TiO}_2$  films in dilute acids (like  $\text{HNO}_3$ ) reduced the concentration of sodium near the surface and improved the efficiency by exchanging sodium ions with protons without degrading the mechanical properties of the  $\text{TiO}_2$  films. The photoefficiency increased particularly in type GN films. Although such soaking was not an adequate substitute for etching the glass prior to the application of the titania precursor, it was an appropriate finishing step for the process of forming a photocatalytic film on soda lime glass.

#### Example 4

##### Preparation of clear photoactive films of titanium dioxide on soda lime glass from coating solutions having controlled viscosities

The coating solution prepared in the manner described in Example 1, (denoted as "Ti" solution in this example) was mixed with various non-interacting organic solvents such as hexane, methylene chloride, chloroform, thus obtaining coating solutions, their viscosities depending upon the volumetric ratio between the coating solution and the non-interacting solvent. For comparison, films made from the "Ti" solution, as well as from a mixture of the "Ti" solution with methanol which may interact, like other alcohols, with the titanium dioxide precursor, were prepared. The mixed solutions were spread on acid - etched glass substrates (40 ml per 3.75x2.5 cm) which were spun, after the application, in  $\text{N}_2$  environment, for 2 minutes at 1000, 2500 or 4000 rpm to dryness. The slides were then calcined at  $400^\circ\text{C}$  for 35 minutes, in air. Clear, homogenous, well adhered films, were obtained.

The photoefficiency of the various types of slides was measured simultaneously. The results are presented in Table 9. For spin coating at 1000 rpm, there was practically no adverse effect on the efficiency following coating by solutions containing a "Ti" / non-interacting solvents mixtures, despite the lower amount of  $\text{TiO}_2$  in these films, due to the reduced viscosity of the coating solution. For spin coating at

2500 rpm, films made of Ti / non-interacting solvents solutions had 30% - 45% of the efficiency of films made of the "Ti" solutions, when illuminated with 365 nm light, and app. 70% - 100% when illuminated with 254 nm light. In contrast, the efficiency, measured with 365 nm light, of TiO<sub>2</sub> films made of the Ti / methanol solution was only 6% of that of the regular GE film when coated at 2500 rpm and 62% when coated at 1000 rpm.

**Table 9**

Slide No.	Coating Solution (v/v)	Solution Viscosity (cp)	Spinning Rate (rpm)	Film Absorbance at 300 nm	Efficiency at 254 nm	Efficiency at 365 nm
1551	Ti/CH <sub>2</sub> Cl <sub>2</sub> (1:1)	0.82	1000	0.94	66.9x10 <sup>-3</sup>	10.9x10 <sup>-3</sup>
1552	Ti/hexane (1:1)	0.88	1000	0.88	81.9x10 <sup>-3</sup>	10.2x10 <sup>-3</sup>
1553	Ti/Chloroform (1:1)	1.16	1000	0.82	70.7x10 <sup>-3</sup>	8.4x10 <sup>-3</sup>
1554	Ti/methanol (1:1)	1.16	1000	0.58	64.1x10 <sup>-3</sup>	6.1x10 <sup>-3</sup>
1555	Ti	2.34	1000	1.09	80.2x10 <sup>-3</sup>	9.8x10 <sup>-3</sup>
1566	Ti/n-propanol (1:1)	1.96	1000	0.57	60.9x10 <sup>-3</sup>	7.4x10 <sup>-3</sup>
1559	Ti/methanol (1:1)	1.16	2500	0.50	43.1x10 <sup>-3</sup>	0.7x10 <sup>-3</sup>
1560	Ti/CH <sub>2</sub> Cl <sub>2</sub> (1:1)	0.82	2500	0.63	66.2x10 <sup>-3</sup>	4.2x10 <sup>-3</sup>
1561	Ti/hexane (1:1)	0.88	2500	0.62	64.4x10 <sup>-3</sup>	5.3x10 <sup>-3</sup>
1562	Ti/Chloroform (1:1)	1.16	2500	0.58	62.7x10 <sup>-3</sup>	3.5x10 <sup>-3</sup>
1563	Ti/n-propanol (1:1)	1.96	2500	0.49	43.8x10 <sup>-3</sup>	5.1x10 <sup>-3</sup>
1564	Ti	2.34	2500	0.71	65.1x10 <sup>-3</sup>	11.9x10 <sup>-3</sup>

10 **Table 9:** Efficiency values of slides prepared by spin coating of mixtures of the TiO<sub>2</sub> precursor coating solution with various non-interacting solvents. In the table, "Ti" represents the regular coating solution, its preparation being described in example 1.

It can be concluded that photoactive clear and homogenous films can be formed on glass by means of diluting the coating solution with solvents that do not interact with the titanium dioxide precursor and that this method is especially viable for cases in which relatively low rates of spinning are required.

**Example 5**  
**Preparation of clear photoactive films of titanium dioxide**  
**on soda lime glass by dip-coating**

Coating solutions of controlled viscosities, prepared in the manner described in example 4, were used to produce clear, photoactive and homogeneous films of  $\text{TiO}_2$  on glass. For that, corning 2947 soda lime glass slides, 7.5x2.5x0.1 cm in size, were etched as described in example 2, connected to a speed controlled elevator and dip coated with an up-stroke speeds ranging between  $0.5 \text{ cm min}^{-1}$  and  $4.3 \text{ cm min}^{-1}$ . The  $\text{TiO}_2$  precursor coated films were then calcined at 400 - 450 °C for 35 minutes. A clear, homogeneous, well adhered film of  $\text{TiO}_2$ , was obtained. Best results, in terms of clarity and homogeneity, were obtained by performing the process under  $\text{N}_2$  atmosphere, enriched with the solvents' vapor. The photoefficiencies of several dip-coated films, as measured by the stearic acid test described in example 1, are presented in table 10.

A comparison between the photoefficiency of the dip - coated films (table 10) and films of similar thickness made by spin coating (Table 2) reveals that the efficiency of the dip-coated films was not inferior to that of the spin-coated films, thus enabling large scale implementation.

**Table 10**

Slide No.	Coating Solution (v/v)	Solution Viscosity (cp)	Up-stroke Speed $\text{cm min}^{-1}$	Calcination	Film Absorbance at 300 nm	Efficiency at 365 nm
1636	Ti/hexane (1:1)	0.88	4.3	400°C, 35 min.	0.65	$12.3 \times 10^{-3}$
1667	Ti/hexane (1:1)	0.88	2.68	450°C, 35 min.	0.57	$11.0 \times 10^{-3}$
1664	Ti <sup>#</sup> /hexane (1:1)	0.9	3.22	450°C, 35 min.	0.55	$9.1 \times 10^{-3}$
1666	Ti/hexane (2:3)	1.02	1.34	450°C, 35 min.	0.61	$8.8 \times 10^{-3}$
1650	Ti/hexane (2:3)	1.02	0.54	450°C, 35 min.	1.13	$13.7 \times 10^{-3}$
1623	Ti/hexane (3:7)	0.66	4.3	400°C, 35 min.	0.28	$5.6 \times 10^{-3}$
1655	Ti <sup>#</sup> /hexane (3:7)	0.65	0.54 (2 layers)	450°C, 35 min.	1.00	$14 \times 10^{-3}$

5 Table 10: Efficiency values of slides prepared by dip-coating in mixtures hexane and the TiO<sub>2</sub> precursor coating solution. In the table, "Ti" represents the regular coating solution, the water to titanium ratio being 11:1, while Ti<sup>#</sup> represents a coating solution where the water to titanium ratio was app. 4:1

### 10 Example 6

#### Preparation of clear photoactive films of titanium dioxide with sodium diffusion limiting layer

15 Silica films were produced on soda lime glass by the same manner described in Examples 1 and 2, using silicon tetrapropoxide instead of titanium tetra-i-propoxide. Here, the silicate precursor solution consisted of 10 ml n-propanol, 1.6 ml acetylacetonate (acac) and 4.9 ml of a Si(OPr)<sub>4</sub> solution (Aldrich Cat. No. 23,574, 95% by weight). The coating solution was made from 1.0 ml of the silicate precursor solution and 1.8 ml of 1:10 (v:v) water in n-propanol. 3.75 cm x 2.5 cm x 1 mm soda  
20 lime glass slides were then etched in boiling sulfuric acid for 30 minutes as described in Example 2, and coated by spin coating as described therein. Following drying at 80°C for 20 minutes, a second layer, made of the same coating solution described in Example

1 (denoted as "overlayer"), was applied by spin coating as described therein. The slides were then calcined at 450°C for 30 minutes to produce clear films comprised of a silica layer (denoted as "underlayer") between the glass substrate and the photoefficient titanium dioxide overlayer. Glass slides coated with a film containing a first layer of zirconia and a second, photoactive layer of titania were obtained in the same manner. Here, the zirconia coating solution was made of zirconium tetra n-propoxide (Aldrich 33,397 -2, 70% in 1-propanol) with the same molar ratios between zirconium, acac, water and propanol as described for the titania precursor coating solution in Example 1. No post-treatment with nitric acid was used.

The efficiency of the slides was measured in the manner described in Example 1. For comparison, films containing one and two layers of TiO<sub>2</sub> on glass, were made from the same batch of etched glass slides and with the same TiO<sub>2</sub> precursor coating solution. The efficiency of these slides was measured simultaneously with that of the glass-silica-titania films. As shown in Table 11, the efficiency of the two layered structure, containing a silica underlayer and TiO<sub>2</sub> overlayer, was higher than that of a single layer of titanium dioxide by a factor of between 1.4 and 2.0, but less than that of a film containing two layers of TiO<sub>2</sub>.

Table 11

Slide No.	Structure	Photoefficiency
701	1 layer of TiO <sub>2</sub> on soda lime glass	3.5 x 10 <sup>-3</sup>
706	1 layer of TiO <sub>2</sub> on soda lime glass	5.6 x 10 <sup>-3</sup>
709	1 layer of TiO <sub>2</sub> on a silica underlayer applied on soda lime glass	8.75 x 10 <sup>-3</sup>
710	1 layer of TiO <sub>2</sub> on a silica underlayer applied on soda lime glass	10.85 x 10 <sup>-3</sup>
699	2 layers of TiO <sub>2</sub> on soda lime glass	14.35 x 10 <sup>-3</sup>
712	2 layers of TiO <sub>2</sub> on soda lime glass	12.95 x 10 <sup>-3</sup>
713	2 layers of TiO <sub>2</sub> on soda lime glass	12.6 x 10 <sup>-3</sup>

A two-layered structure, consisting of a zirconia underlayer and one TiO<sub>2</sub> overlayer coated on glass, had higher efficiency than that of a glass coated with a single film of TiO<sub>2</sub>, when made at calcination temperatures higher than 500°C, where the

diffusion of sodium into the forming  $\text{TiO}_2$  film is fast enough to reduce its efficiency even in acid etched glass substrates (Figure 4). This makes such a sodium diffusion blocking structure appropriate for applications where the glass has to withstand high temperatures, for example in products made by tempering of the glass.

5

### Example 7

#### Preparation of clear photoactive films of titanium dioxide on a layer made of a mixture of a $\text{TiO}_2$ precursor and a $\text{SiO}_2$ precursor

10

A layer composed of a mixture of  $\text{TiO}_2$  and  $\text{SiO}_2$  (1:1) molar ratio was produced on soda lime glass and on fused silica by preparing the appropriate coating solution and applying it onto the substrate by spin coating as described in examples 1 and 2. A precursor solution was made of 10 ml n-propanol, 2.25 ml titanium-tetra-i-propoxide (98% in propanol, density:  $1.033 \text{ gr. cm}^{-3}$ ), 1.6 ml acetylacetonate (acac) and 2.43 ml of silicon tetrapropoxide (Aldrich 23,574-1, 95% in propanol, density:  $0.916 \text{ gr. cm}^{-3}$ ). After aging the precursor solution for a day, the coating solution was made by mixing 1.0 ml of the mixed precursor solution with 1.8 ml of a water/ n-propanol solution (1:10 v/v). The coating solution was then spread by spin coating at 4000 rpm on  $\text{H}_2\text{SO}_4$  etched glass slides (40  $\mu\text{l}$  per  $3.75 \times 2.5 \text{ cm}$  slide) and on non-etched fused silica slides (30  $\mu\text{l}$  per  $2.5 \times 2.5 \text{ cm}$  slide). The slides were then dried in an oven at  $100^\circ\text{C}$  for 10 minutes. On part of the slides, a second layer, consisting of the  $\text{TiO}_2$  precursor coating solution, mentioned in Example 1, was applied in the same manner described in Examples 1,2. For reference, several other etched glass and fused silica slides were coated with two layers of the same  $\text{TiO}_2$  precursor coating solution without being coated with the mixed underlayer. All slides were then calcined at  $450^\circ\text{C}$  for 30 minutes to produce clear, well adhered films. No post-treatment with nitric acid was used.

The efficiency of the slides was measured in the manner described in Example 1. The films made of the  $\text{TiO}_2/\text{SiO}_2$  mixture were totally inactive. However, films consisting of a  $\text{TiO}_2$  overlayer on an inactive underlayer consisting of  $\text{TiO}_2/\text{SiO}_2$  were found to be between 50% and 100% more efficient than films made of one layer of  $\text{TiO}_2$ , regardless of the substrate (Table 12).

30

Table 12

Slide No.	Substrate	Structure	Efficiency
A	Fused Silica	Mixed SiO <sub>2</sub> /TiO <sub>2</sub> (1:1) layer	0.3 x 10 <sup>-3</sup>
B	Fused Silica	Mixed SiO <sub>2</sub> /TiO <sub>2</sub> (1:1) layer	1.7 x 10 <sup>-3</sup>
C	Fused Silica	One layer of TiO <sub>2</sub> on a mixed SiO <sub>2</sub> /TiO <sub>2</sub> (1:1) layer	13.7 x 10 <sup>-3</sup>
D	Fused Silica	One layer of TiO <sub>2</sub> on a mixed SiO <sub>2</sub> /TiO <sub>2</sub> (1:1) layer	16.1 x 10 <sup>-3</sup>
E	Fused Silica	One layer of TiO <sub>2</sub>	4.9 x 10 <sup>-3</sup>
F	Fused Silica	One layer of TiO <sub>2</sub>	9.0 x 10 <sup>-3</sup>
G	Fused Silica	Two layers of TiO <sub>2</sub>	13.1 x 10 <sup>-3</sup>
H	Fused Silica	Two layers of TiO <sub>2</sub>	17.2 x 10 <sup>-3</sup>
684	Etched Glass	Mixed SiO <sub>2</sub> /TiO <sub>2</sub> (1:1) layer	0.0 x 10 <sup>-3</sup>
685	Etched Glass	Mixed SiO <sub>2</sub> /TiO <sub>2</sub> (1:1) layer	0.0 x 10 <sup>-3</sup>
1711	Etched Glass	One layer of TiO <sub>2</sub> on a mixed SiO <sub>2</sub> /TiO <sub>2</sub> (1:1) layer	16.6 x 10 <sup>-3</sup>
1712	Etched Glass	One layer of TiO <sub>2</sub> on a mixed SiO <sub>2</sub> /TiO <sub>2</sub> (1:1) layer	16.7 x 10 <sup>-3</sup>
1701	Etched Glass	One layer of TiO <sub>2</sub>	8.6 x 10 <sup>-3</sup>
1702	Etched Glass	One layer of TiO <sub>2</sub>	8.6 x 10 <sup>-3</sup>
1707	Etched Glass	Two layers of TiO <sub>2</sub>	18.7 x 10 <sup>-3</sup>
1708	Etched Glass	Two layers of TiO <sub>2</sub>	17.4 x 10 <sup>-3</sup>

Table 12: The photoefficiencies of films composed of one TiO<sub>2</sub> layer on a silica/titania underlayer in comparison to films made of one TiO<sub>2</sub> layer, two TiO<sub>2</sub> layers, and a mixture of TiO<sub>2</sub>/SiO<sub>2</sub>.

**We claim:**

1. A process for the manufacture of self-cleaning glass, comprising:  
applying to glass a photocatalyst precursor composition to form a  
5 photocatalyst-containing film; and  
impeding migration of alkali metal ions or alkali metal oxide from the  
glass into the photocatalyst precursor or film.
2. A process for the manufacture of self-cleaning glass, comprising:  
10 applying to glass a barrier, said barrier preventing or slowing migration  
of alkali metal ions or alkali metal oxide from the glass; and  
forming on said barrier a photocatalyst-containing film.
3. A process for the manufacture of self-cleaning glass, comprising:  
15 applying to an etched, acid glass a photocatalyst precursor composition,  
to form a photocatalyst-containing film.
4. A process for the manufacture of self-cleaning glass, comprising:  
applying to glass a film formed of a precursor of  $\text{TiO}_2$  and a precursor of  
20 an oxide of a 3, 4, or 5-valent element, which oxide is solid at about  $300^\circ\text{C}$ ; and  
forming on said film a photocatalyst-containing film.
5. A process for the manufacture of self-cleaning glass, comprising:  
applying to an acid glass a first film, the first film formed from a  
25 precursor of an oxide of a 3, 4, or 5-valent element, wherein the element is titanium,  
zirconium, tungsten, tin, silicon, or combination thereof; and  
forming on said first film a photocatalyst-containing second film.
6. A process for the manufacture of self-cleaning glass, comprising:  
30 applying to acid glass a film comprising a reaction product of the  
acid glass and a precursor of a 3, 4, or 5-valent form of titanium, zirconium, tungsten,  
tin, silicon, or combination thereof; and

forming on said barrier a photocatalyst-containing film.

7. A process for the manufacture of self-cleaning glass, comprising:  
treating glass to form acid glass;  
5 applying a photocatalyst-precursor to the acid glass to form a coated  
glass;  
calcining the coated glass to form a photocatalytically active, self-  
cleaning glass.
- 10 8. A process according to any of claims 1-7, wherein said photocatalyst comprises  
a photoconductor or semiconductor with a band gap in the range of 2.5 eV to 4.5 eV.
9. The process according to any of claims 1-7, wherein said photocatalyst  
comprises titanium, zirconium, tungsten, tin, or molybdenum.
- 15 10. A process according to any of claims 1-7, wherein said photocatalyst comprises  
titanium dioxide.
11. A process according to claim 10, wherein at least a portion of said titanium  
20 dioxide is in anatase phase.
12. The process of any of claims 1-6, further comprising the step of:  
calcining the photocatalyst film-coated glass to form a photocatalytically  
active, self-cleaning glass.
- 25 13. A process according to any of claims 1-7, wherein said glass comprises soda  
lime glass.
14. A process according to claim 6, wherein said precursor comprises a precursor of  
30 titanium dioxide.

15. A process according to claim 6, wherein said precursor comprises a precursor of zirconium dioxide.

5 16. A process according to claim 6, wherein said precursor comprises a precursor of silicon dioxide.

17. A self-cleaning glass comprising:  
a glass;  
a photocatalyst-containing film formed on the glass from a photocatalyst  
10 precursor; and  
a barrier impeding migration of alkali metal ions or alkali metal oxides into the photocatalyst precursor or film.

18. A self-cleaning glass comprising:  
15 a glass;  
a photocatalyst-containing film formed on the glass by acid etching the glass and applying to the acid glass a photocatalyst precursor.

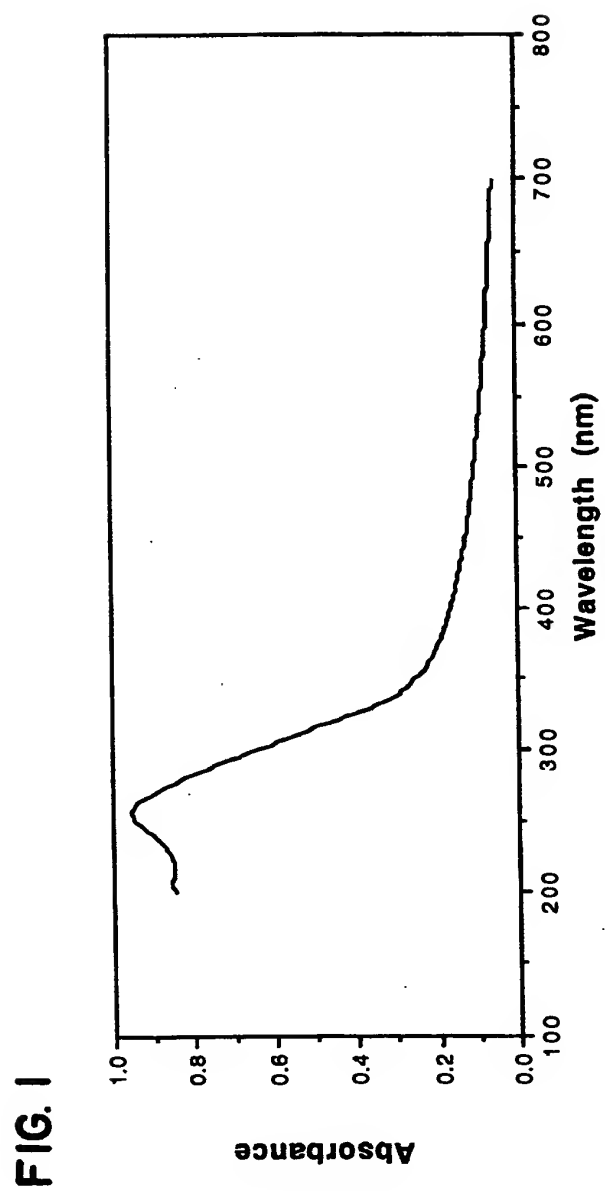
19. A self-cleaning glass comprising:  
20 a glass;  
a first film formed on the glass of a precursor of  $\text{TiO}_2$  and a precursor of an oxide of 3, 4, or 5-valent element, which oxide is solid at about  $300^\circ\text{C}$ ; and  
a photocatalyst-containing second film formed on the first film.

25 20. A self-cleaning glass comprising:  
a glass;  
a first film formed on the glass of a precursor of an oxide of a 3, 4, or 5-valent element, wherein the element comprises titanium, zirconium, tungsten, tin, silicon, or combination thereof; and  
30 a photocatalyst-containing second film formed on the first film.

21. A self-cleaning glass according to any of claims 17-20, wherein said photocatalyst comprises a photoconductor or semiconductor with a band gap in the range of 2.5 eV to 4.5 eV.
- 5 22. A self-cleaning glass according to any of claims 17-20, wherein said photocatalyst comprises titanium, zirconium, tungsten, tin, or molybdenum.
23. A self-cleaning glass according to any of claims 17-20, wherein said photocatalyst comprises titanium dioxide.
- 10 24. A self-cleaning glass according to claim 23, wherein at least a portion of said titanium dioxide is in anatase phase.
25. A self-cleaning glass according to any of claims 17-20, wherein said  
15 photocatalyst precursor is calcined on the glass to form a photocatalytically active, self-cleaning glass.
26. A self-cleaning glass according to any of claims 17-20, wherein said glass  
comprises soda lime glass.
- 20 27. A self-cleaning glass according to any of claims 19-20, wherein said precursor of the 3, 4, or 5-valent element oxide comprises a precursor of zirconium dioxide.
28. A self-cleaning glass according to any of claims 19-20, wherein said precursor  
25 of the 3, 4, or 5-valent element oxide comprises a precursor of silicon dioxide.
29. A self-cleaning glass according to any of claims 17-20, wherein said photocatalyst precursor comprises titanium tetraalkoxide.
- 30 30. A self-cleaning glass according to any of claims 17-20, wherein said photocatalyst precursor comprises a complex of titanium tetraalkoxide with acetylacetone.

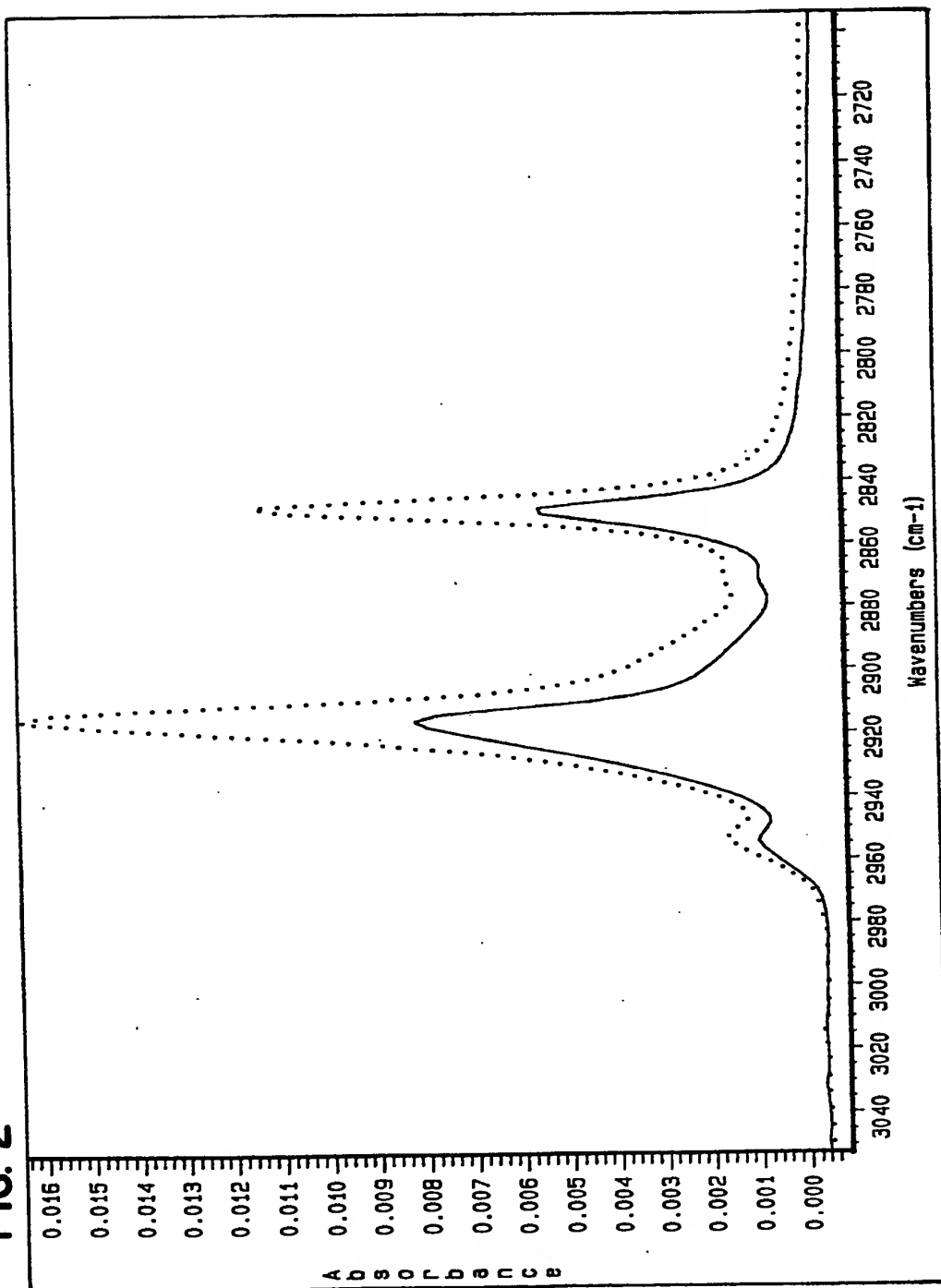
31. A self-cleaning glass according to claim 17, wherein said barrier comprises a reaction product of the glass and the photocatalyst precursor, the glass being etched to form an acid glass prior to the reaction with the precursor.

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FIG. 2



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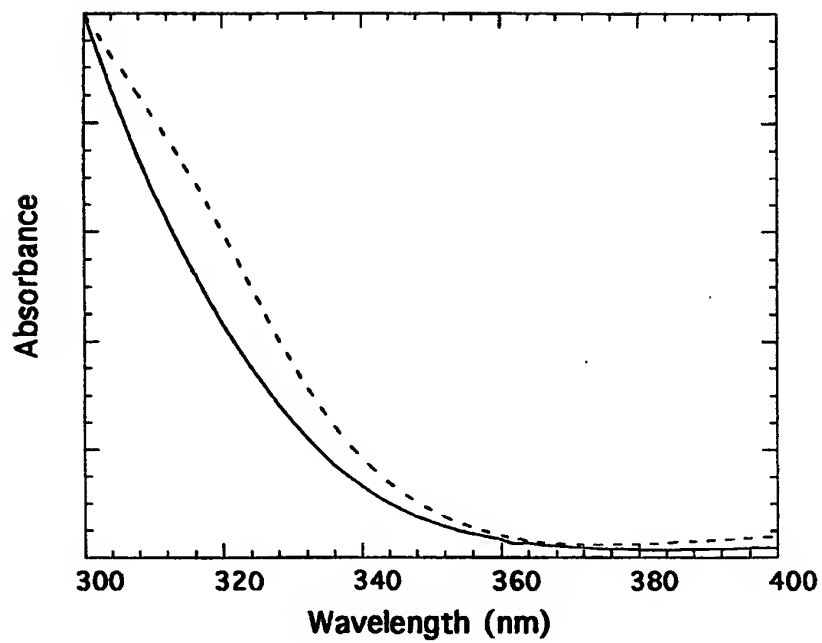


FIG. 3

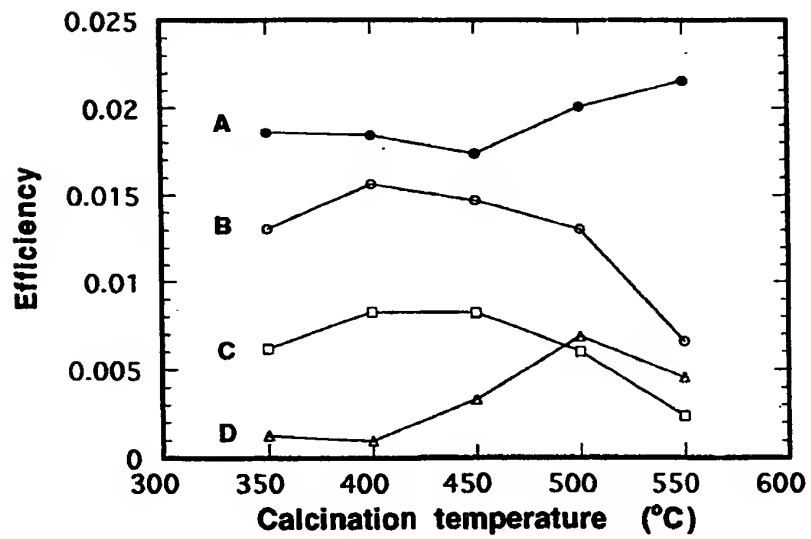


FIG. 4

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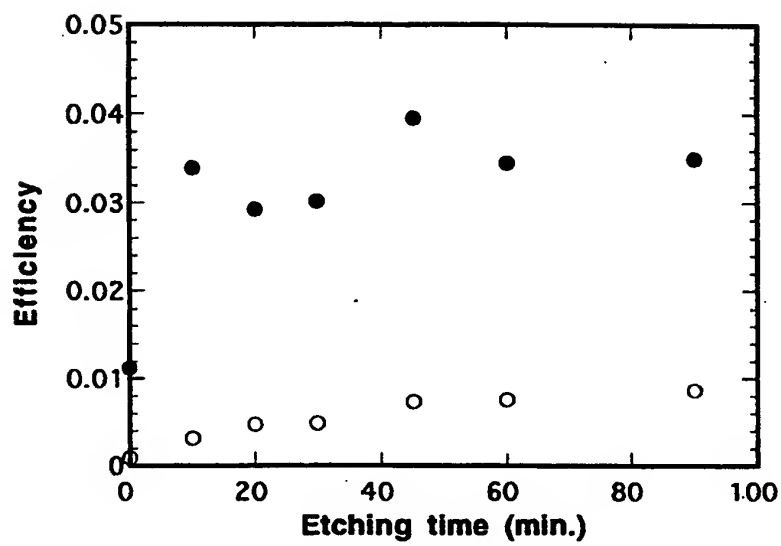


FIG. 5

# INTERNATIONAL SEARCH REPORT

Int. Application No  
PCT/US 96/12792

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C03C17/34 C03C17/25 C03C23/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	EP,A,0 684 075 (TOTO LTD) 29 November 1995	1,2, 8-13,17, 21-26, 29,30
P,Y	see page 9, line 7 - line 36; example 35	3,7,18, 31
X	& WO,A,95 15816 (TOTO LTD) 15 June 1995	1,2, 8-13,17, 21-26, 29,30
Y		3,7,18, 31
Y	GB,A,2 206 878 (GLAVERBEL) 18 January 1989 see abstract	3,7,18, 31
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

15 November 1996

Date of mailing of the international search report

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
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# INTERNATIONAL SEARCH REPORT

Inter. Application No  
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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A	<p>PATENT ABSTRACTS OF JAPAN vol. 018, no. 625 (C-1279), 29 November 1994 &amp; JP,A,06 239650 (NIPPON TAISANBIN KOGYO KK), 30 August 1994, see abstract</p> <p style="text-align: center;">---</p>	1-31
A	<p>EP,A,0 174 727 (PILKINGTON BROTHERS PLC) 19 March 1986 see abstract</p> <p style="text-align: center;">---</p>	1-31
A	<p>SZKLO I CERAMIKA, vol. 43, no. 6, 1992, POLAND, pages 2-7, XP002018688 ZELAZOWSKA: "Study of metal oxide and titanium oxynitride coatings on soda-lime glass" see page 5, left-hand column see page 7, left-hand column</p> <p style="text-align: center;">-----</p>	1-31

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Information on patent family members

Intr Application No

PCT/US 96/12792

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